965,351

PATENT SPECIFICATION

NO DRAWINGS

965,351

Date of Application and filing Complete Specification: Dec. 4, 1962.

No. 45807/62.

Application made in United States of America (No. 163,091) on Dec. 29, 1961.

Complete Specification Published: July 29, 1964.

© Crown Copyright 1964.

Index at acceptance:—C2 C(2A2, 2B20, 2T16)

International Classification:—C 07 c

COMPLETE SPECIFICATION

Purification of Unsaturated Nitriles

We, THE STANDARD OIL COMPANY, a corporation organised under the laws of the State of Ohio, United States of America, of Midland Building, Cleveland 15, Ohio, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the purification of unsaturated nitriles such as acrylonitrile and methacrylonitrile, to separate them from small amounts of hydrogen cyanide.

When an olefin, such as propylene or isobutylene is reacted with ammonia and oxygen to produce the corresponding unsaturated nitriles such as acrylonitrile or methacrylonitrile, there is also produced substantial amounts of hydrogen cyanide and trace amounts of carbonyl compounds of relatively low molecular weight, such as acetaldehyde, propionaldehyde, acrolein, methacrolein, acteone and methyl ethyl ketone.

The separation of the hydrogen cyanide presents troublesome problems because it combines with the carbonyl compounds to form cyanhydrins. These cyanhydrins decompose to hydrogen cyanide and the corresponding carbonylic compound under some operating conditions, and recombine to form the cyandydrin under other conditions so that it is difficult to eliminate the hydrogen cyanide. Because of its objectionable nature, hydrogen cyanide must be eliminated from the nitrile produced.

We have discovered that the cyanhydrins can be effectively stabilised and the above-mentioned decomposition can be suppressed by the addition of small amounts of oxalic acid to the unsaturated nitrile containing the cyanhydrins. The oxalic acid is superior to phosphoric acid, sulphuric acid, acetic acid and similar acids in that it does not form sludges which is the case with the mineral acids, and it is the proper strength to stabilise the cyanhydrins, which is not the case with most organic acids.

Accordingly the present invention provides a process for purifying an unsaturated nitrile containing hydrogen cyanide in the form of a cyanhydrin which normally tends to decompose during the distillation of the unsaturated nitrile and contaminate the distilled produce with the hydrogen cyanide, which comprises adding to the unsaturated nitrile 0.001 to 0.1 pound of oxalic acid per 100 pounds of unsaturated nitrile, and distilling the nitrile in the presence of the oxalic acid.

According to a preferred embodiment the present invention provides a process for purifying acrylonitrile which comprises feeding to a fractional distillation column near the bottom of said column a liquid stream of acrylonitrile containing hydrogen cyanide in the form of a cyanhydrin, and from 0.001 to 0.1 pound of oxalic acid per 100 pounds of acrylonitrile vaporising a portion of the liquid from the bottom of the column and condensing the overhead vapours and retaining at least a portion of the condensate in the column and withdrawing near the top of the column a sidestream of purified acrylonitrile.

The present invention is preferably carried out as follows:

A stream of acrylonitrile containing trace amounts (0.01% by weight) of hydrogen cyanide as cyanhydrins which is to be purified, is fed into a fractionating column which is equipped with a reboiler at the bottom, a condenser for the vapours taken overhead, and means for returning most of the condensate to the column as reflux. Means are provided for purging a portion of the condensate periodically from which low boiling components may be stripped and the stripped acrylonitrile added to the reflux. Means are also provided to withdraw, continuously or periodically, a portion of the contents of the

[*Price 4s. 6d.*]

reboiler and the acrylonitrile can be stripped therefrom and returned to the fractionating column leaving the cyanhydrins and other heavy boiling components. A side stream near the top of the column, preferably about one-fourth of the way from the top, is provided, from which the cyanide-free acrylonitrile may be withdrawn. A feed stream is provided near the centre or the bottom of the column from which the acrylonitrile to be purified is fed. The oxalic acid may be introduced into this feed stream or at any point in the column below the product take-off stream or in the reboiler, but it is most convenient to add it either continuously or periodically.

The oxalic acid can be added in any form but is most conveniently added as an aqueous solution, preferably concentrated or saturated, although solid oxalic acid may also be introduced. The oxalic acid may also be dissolved in a portion of the acrylonitrile to be purified and this stream added to the crude acrylonitrile stream to be purified.

The amount of oxalic acid added either continuously or periodically is in the ratio of 0.001 to 0.1 pound of oxalic acid per 100 pounds of acrylonitrile feed to the column. Under these circumstances, the hydrogen cyanide is effectively combined and stabilised as the cyanhydrin and the side stream withdrawn near the top of the column contains little, usually less than 10 parts per million, of titratable cyanide.

WHAT WE CLAIM IS:—

1. A process for purifying an unsaturated nitrile containing hydrogen cyanide in the form of a cyanhydrin which normally tends to decompose during the distillation of the unsaturated nitrile and contaminate the distilled product with hydrogen cyanide, which comprises adding to the unsaturated nitrile 0.001 to 0.1 pound of oxalic acid per 100 pounds of unsaturated nitrile, and distilling the nitrile in the presence of the oxalic acid.

2. A process for purifying acrylonitrile which comprises feeding to a fractional distillation column near the bottom of said column a liquid stream of acrylonitrile containing hydrogen cyanide in the form of a cyanhydrin and from 0.001 to 0.1 pound of oxalic acid per 100 pounds of acrylonitrile vaporising a portion of the liquid from the bottom of the column and condensing the overhead vapours and retaining at least a portion of the condensate in the column and withdrawing near the top of the column a side stream of purified acrylonitrile.

3. A process for purifying an unsaturated nitrile substantially as described.

4. Purified unsaturated nitriles when obtained by the process claimed in any one of the preceding claims.

ELKINGTON & FIFE,
Chartered Patent Agents,
Bank Chambers, 329, High Holborn,
London, W.C.1,
Agent for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press (Leamington) Ltd.—1964. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.